

**SYNTHESIS AND CHARACTERIZATION OF MOLECULES FOR ELECTRON-
TRANSFER RESEARCH**

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Dimethoxynaphthalene (donor) and quinone (acceptor) have been chosen as a suitable redox pair and are bonded to either permethylated silane chains or corresponding permethylated alkyl chains to form Acceptor-(Bridge)-Donor molecules. The idea that the σ -delocalization phenomenon of silane chains may greatly facilitate ET reactions will be tested. The starting material for the donor precursor, 4-(1,4-dimethoxynaphthyl)bromocyclohexane, was 1,4-naphthoquinone. After methylation and bromination, the Grignard reagent of the resulting bromide was reacted with cyclohexanedione, *mono* ethylene ketal. The resulting alcohol was changed to the donor precursor through the following functional group transformation steps: dehydration, hydrogenation, deketalization and bromination. 1,4-Dibenzyloxybromobenzene, the precursor for the acceptor, was synthesized from 1,4-hydroquinone through bromination and benzylation. The connection of the two precursors and either permethylated silane chains or permethylated alkyl chains will give the final target molecules for ET research. Progress on this is included.

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I INTRODUCTION

Remarkable progress has been made in the experimental and theoretical elucidation of the processes of chemical energy acquisition, storage, and disposal in large molecules, clusters, condensed phases, and biological systems. This broad area plays an important role in the development of modern chemistry. A major goal of these diverse and important fields pertains to a unified description of structure-energy-spectroscopic-dynamic relations and correlations. Electron-transfer (ET) processes provide a central case of intramolecular, condensed-phase, and biophysical dynamics [1-27].

Since ET processes constitute ubiquitous and fundamental phenomena in chemistry, physics, and biology, they have long drawn great attention. A theory developed about thirty years ago predicted that in ET processes if the donor (D) and the acceptor (A) were separated by a long distance, the electron moves from D to A via a through-bond mechanism. This mechanism is called “superexchange” in which the wave functions of the spacer (Sp) or bridge (Br) engage the ET process and help facilitate the electron or charge transfer. This through-bond tunneling was predicted to increase the ET reaction rate dramatically, compared to a corresponding through-space transfer.

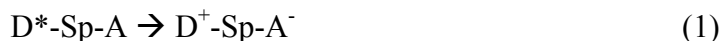
Due to the complexity of approaching the nature of these processes in the real world, some methodologies were developed to simplify the problem and verify the basic theories and predictions. The most thoroughly studied D-(bridge)-A molecules have been those with saturated organic bridges. This modeling gives a better simulation for complicated biological systems in which there is often an unchanging distance between the electron donor and acceptor.

In our research, we choose catenated heavy group 14 atom chains instead. These chains show a remarkable σ -delocalization phenomenon, which makes heavy group 14 atom chains more reminiscent of conjugated organic polyenes than saturated hydrocarbons. π -Conjugated systems indeed have been reported to function as molecular wires in ET processes in comparison to saturated hydrocarbons [28]. Thus catenated heavy group 14 atom chains were envisaged to greatly facilitate ET reactions.

I.1 Basic theory of long-distance ET reactions

In recent years, some research groups realized that intramolecular ET reactions in molecules, in which the electron acceptor and electron donor are connected by an inert rigid spacer (Sp) or bridge (Br), give definite advantages over freely diffusing systems. Foremost the distance of the electron movements has been restrictedly defined [29-33]. Also such systems are obviously better to model biological ET processes that commonly involve an electron donor and an electron acceptor bound by a fixed distance and a fixed orientation.

Equations shown below represent the systems in which we are interested here.



The rate k for ET reactions like other reactions can be presented by an Arrhenius expression [34] (Eq. 3) with the preexponential factor A and an exponential temperature (T) dependence, the magnitude of which depends on an activation energy (E_a).

$$k = A \exp[-E_a/k_B T] \quad (3)$$

In Eyring's[35] transition state theory (TST), A is replaced by $\kappa k_B T/h$, where κ is the transmission coefficient, h is Planck's constant and k_B is Boltzmann's constant. Also the activation energy is replaced by the free energy of activation (ΔG^\ddagger) (Eq. 4).

$$k = \kappa k_B T/h \exp[-\Delta G^\ddagger/k_B T] \quad (4)$$

The intramolecular ET interactions, of interest here, between A and D presented by Equation 1 and 2 are extremely weak ($\ll 1$ kilocalorie), compared with energies of bond formation or cleavage. In most cases, the solvent around the molecules is the major environmental factor besides the temperature on intramolecular ET reactions. It is clear that when electron moves upon the molecular framework the polarity and charge of the molecule change and the polarity and charge distribution of the solvent molecules will change correspondingly.

Forty years ago, Marcus predicted the relationship between the solvent reorganization energy (λ_s), which represents the interaction between molecules and solvent, and the free energy of activation ΔG^\ddagger [36]. This is given in the following equation:

$$\Delta G^\ddagger = (\Delta G^0 + \lambda_s)^2/4\lambda_s \quad (5)$$

where ΔG^0 is the free energy difference between starting materials and products. Thus equation 4 can be changed to equation 6.

$$k_{ET} = \kappa k_B T/h \exp[-(\Delta G^0 + \lambda_s)^2/4\lambda_s k_B T] \quad (6)$$

A very interesting property of ET reactions can be drawn from the equation 5: as the driving force of the reactions increases and the free energy becomes more negative, the reaction rate rises to a maximum where $\lambda_s = -\Delta G^0$, and then drops off again. This unexpected classic prediction is called "inverted region" which is the most counterintuitive and controversial result in Marcus theory.

Early tests on this theory were unsuccessful and few cases seemed to show the inverted region. This variance was thought to be mainly due to two reasons: first, intermolecular reactions were selected to simulate intramolecular ones and the interaction of the reactants depended on diffusion instead of molecular structure; second, very exoergic reactions were chosen, which allowed product formation in the excited states to give artificially high rates. Recent studies [37, 38] have corrected those deviations and shown an inverted region.

The distance from the electron donor to acceptor is another important factor in ET reaction. Here a question arises about how electron moves from one edge of the molecules to another. The through space mechanism, which is simply by the overlap of A/D wave functions through space, is not accepted due to the many reports about edge-to-edge distances between donor and acceptor of over 15 Å still giving rates in the nanosecond regime. Such long range ET researches support the through-bond mechanism or superexchange coupling in which the wave-function of the spacer couples those of A and D. The bridge states interact with each other and with the D and A states so that the overall D/A coupling is much greater than the corresponding direct (through space) D/A coupling. As this energy gap, or tunneling energy, decreases between the bridge and the D and A, ET rates are predicted by theory to increase dramatically.

Our research will test the theories mentioned above by designing specific molecules and analyzing the ET rates of these molecules.

I.2 σ -delocalization phenomenon of heavy group 14 elements

Kipping completed the first successful syntheses of polysilane derivatives in the early 1920s by condensing diphenyldichlorosilane with sodium [39]. These materials however attracted little interest for many years since they were infusible and intractable. This was one cause for the lack of the methodology for the syntheses of polymers backboned by heavy group 14 atoms (Si, Ge, and Sn). Until the last decade, a very strong motivation to remedy this situation came from more and more evidence that suggested that a large amount of various structural classes of these compounds could have unusual and interesting properties.

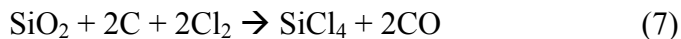
For instance, the linear polystannanes in general formula $R(SnR_2)_nR$ (R = alkyl or aryl) can be formally considered as heavy-atom structural analogs of saturated hydrocarbons, $H(CH_2)_nH$. An investigation of the electronic spectra for a homologous series of above compounds (e.g., $n = 1-6$) shows that they more closely resemble unsaturated conjugated polyenes due to the occurrence of a remarkable intense low-energy absorption maximum which red-shifts when the chain length increases [40]. Similar behaviors were observed for both polysilanes and polygermanes.

INDO/S calculations [41] predicted this low-energy absorption corresponds to a $\sigma - \sigma^*$ transition (HOMO \rightarrow LUMO) of the backbonded heavy group 14 chains instead of a substituent effect. This $\sigma -$ delocalization phenomenon is an intrinsic property of the catenated chains of σ -bonded group 14 heavy atoms [42].

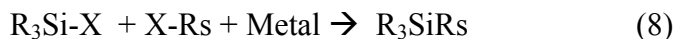
I.3 Background of silane coupling reaction

Unlike carbon based organic compounds which are very common, there is no natural organic silicon compound; all known examples were created in the chemical laboratory.

The very first starting material for most organic silicon compounds is silicon tetrachloride which is normally made by the following reaction:



Obviously how to change the Si-Cl bond to a Si-C bond is the key for syntheses of organic silicon compounds. Normally such transformations have been achieved (Eq. 9) by reacting silane halides with organometallic compounds or organic halides with metals as catalyst [43].



(R, Rs = organic group, X = halide)

I.4 Target molecule design and experimental methods

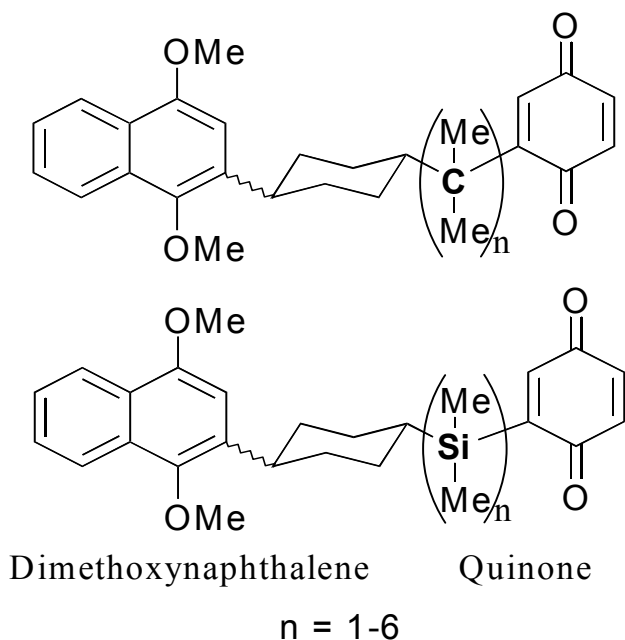


Figure 1

The proposed series of compounds for the ET distance-dependence research are shown as **Figure 1**.

Dimethoxynaphthalene and quinone have been chosen as a suitable donor/acceptor pair based on work of others [44, 45]. We introduce the inert cyclohexyl spacers to ensure rigidity due to the partial flexibility of the

permethylated σ -bond connected group 14 element chains; the cyclohexyl spacer will prevent face-to-face interaction between D and A from happening.

The influence of geometric differences on ET rate will be interesting and tested; the proposed synthetic path will make both e,e and e,a isomers. Several different solvents will be used to help determine the Franck-Condon factors [46].

After the syntheses of the compounds with one to six heavy group 14 atom chains between donor and acceptor, it will be straightforward to differentiate the effects of tunneling through heavy group 14 atom chains from the differences in their coupling to the organic moieties. It will be of interest to see if the compounds with catenated heavy group 14 atoms give faster ET rate than their organic analogs even though the edge-to-edge distance of the former cases are longer. The distance factor will be the key to measure the effect of the σ -delocalization on ET reactions.

II RESULTS AND DISCUSSION OF SYNTHESSES

II.1 SYNTHETIC STRATEGIES:

The proposed strategies are based on published methodology. It is clear that all the target molecules are from same two precursors (**10**) and (**12**) (**Figure 2**) which are

connected to different permethylated chains of either carbon atoms or silicon atoms.

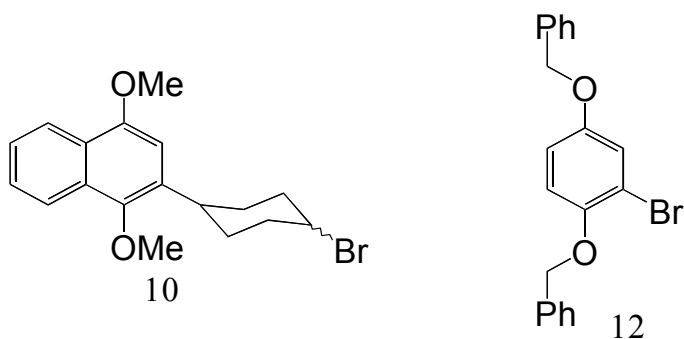
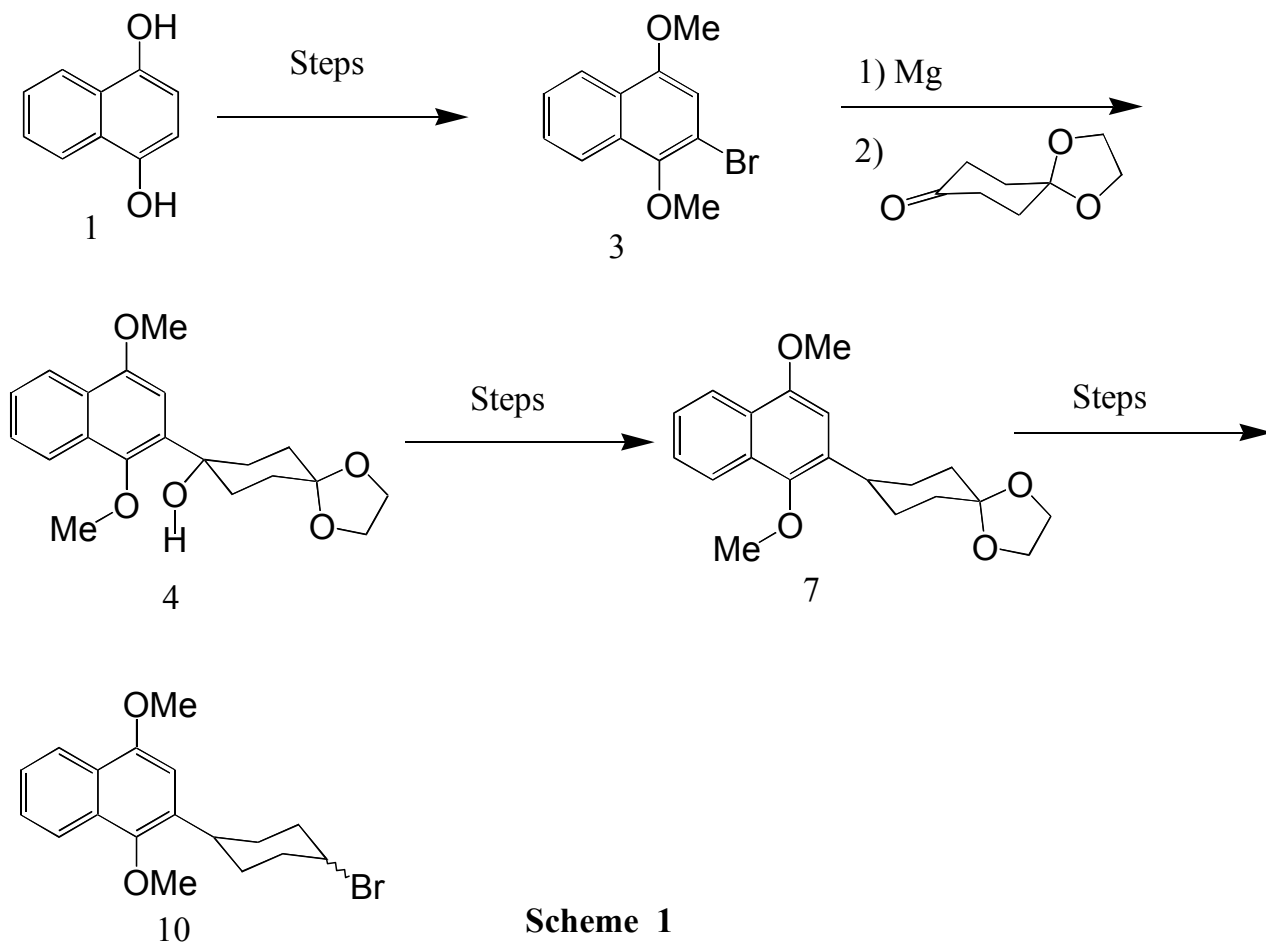


Figure 2

The precursor (**10**) for electron donor part is a 4-(1,4-dimethoxynaphthyl)cyclohexyl halide which can be synthesized from 1,4-dihydroxynaphthalene as shown in **Scheme 1**.

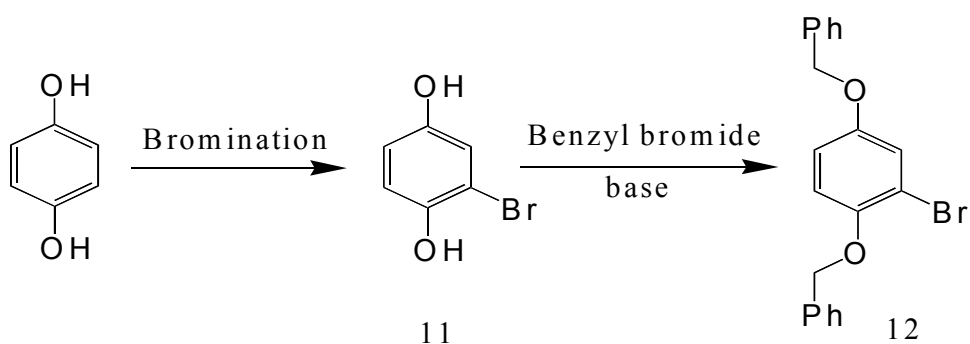


Scheme 1

After a methylation and an aromatic bromination of (**1**), the product, 1,4-dimethoxy-2-bromonaphthalene (**3**) will be transformed to either a Grignard or lithium reagent and

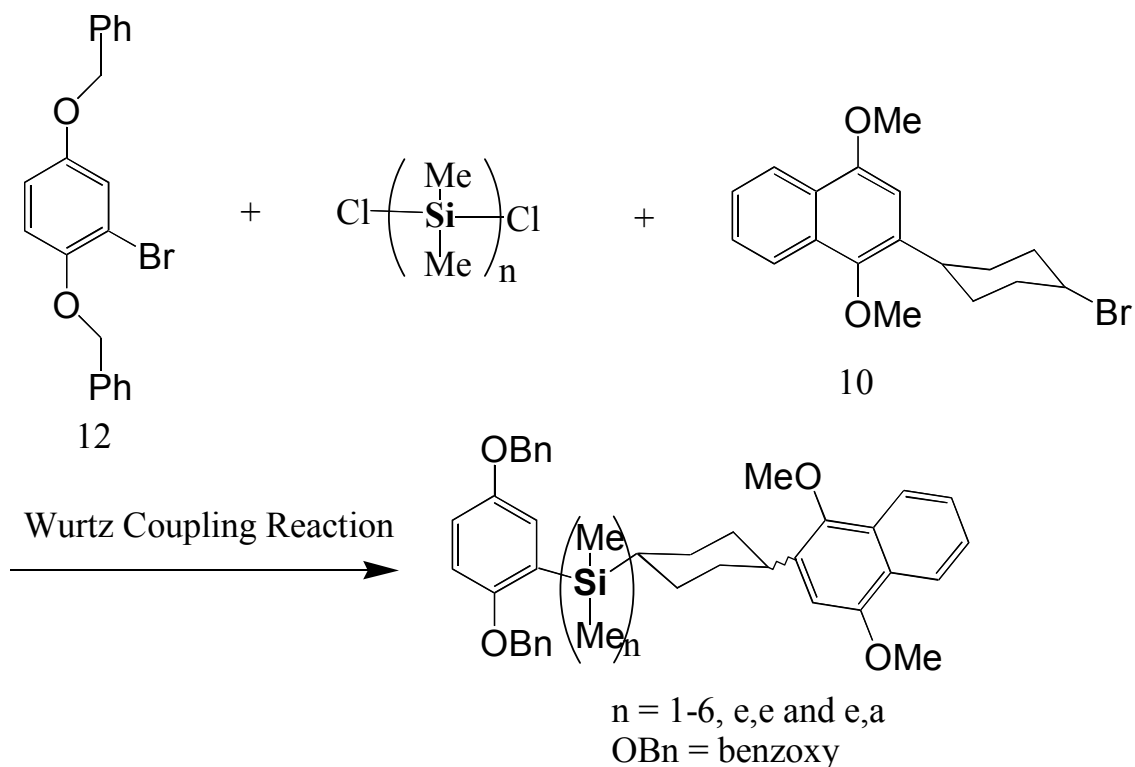
connected to 1,4-cyclohexanedione, *mono* ethylene ketal. The following alcohol (**4**) can then be dehydrated and hydrogenated to remove the hydroxy group and the ketal (**7**) will be formed. Acid catalyzed deketalization of the ketal (**7**) followed by similar standard functional group manipulation will lead to the desired halide (**10**).

The precursor for the electron acceptor part of the target molecule is the bromide (**12**) of dibenzyloxybenzene which can be synthesized through bromination and benzylation from 1,4-hydroquinone as shown in **Scheme 2**.



Scheme 2

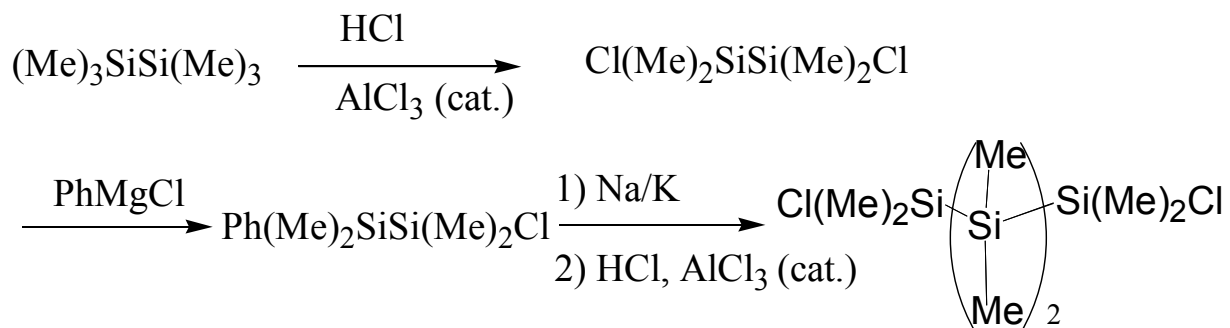
For the silicon series of target molecules (**Scheme 3**), the two



Scheme 3

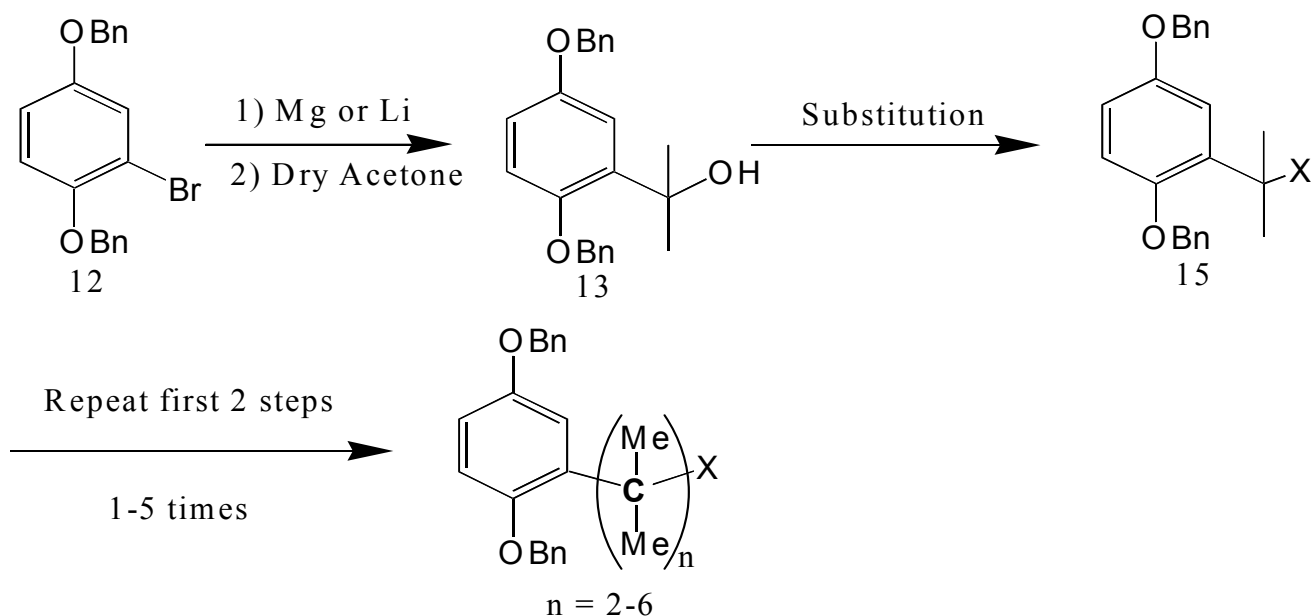
precursors can be used in a stoichiometric Wurtz-type coupling reaction [47] with permethylated dichlorosilane derivatives. With good control, two different halides can be connected on both sides of the silane chain.

Permethylated dichlorosilanes with various numbers of silicon atoms either are commercially available or will be synthesized from commercially available hexamethyldisilane by known methods (**Scheme 4**).



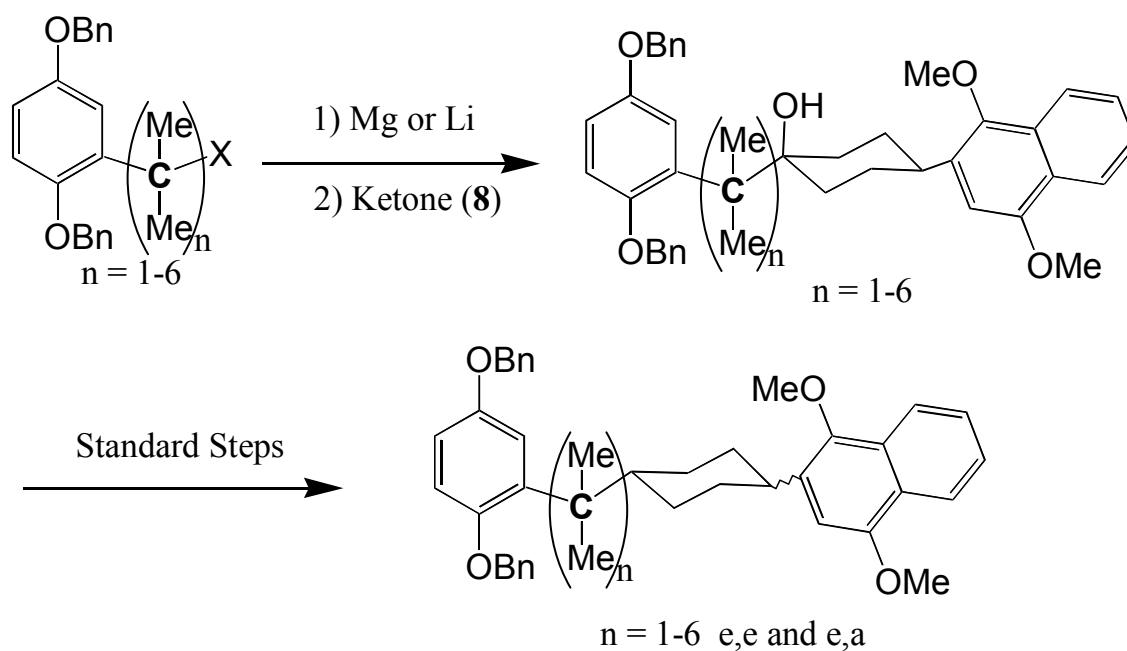
Scheme 4

For the permethylated alkyl-chained target molecules, methods involving one carbon prolongation of the chain by organometallic reactions with acetone such as that shown in **Scheme 5** will be used.



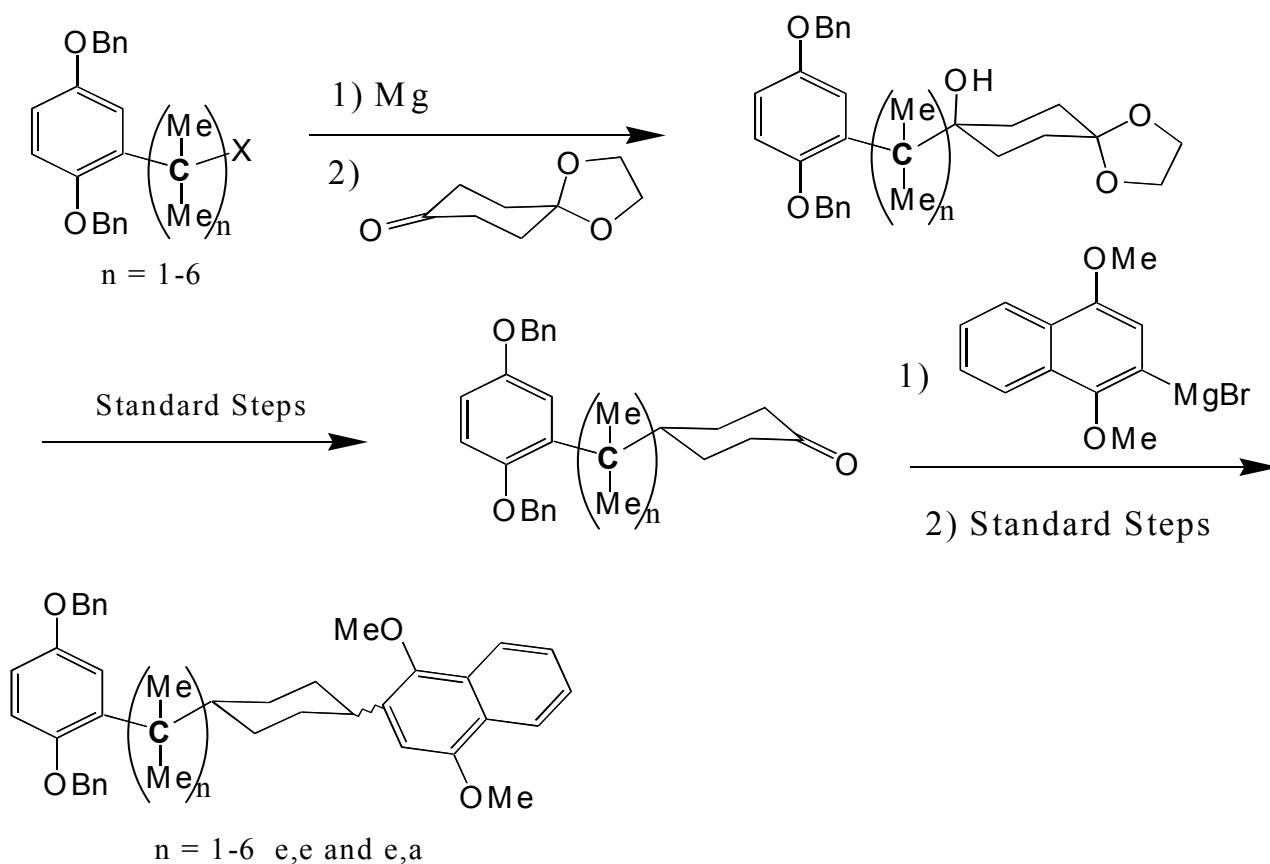
Scheme 5

The resulting halides will be reacted with 4-(1,4-dimethoxy-2-naphthyl)-cyclohexanone (**8**).



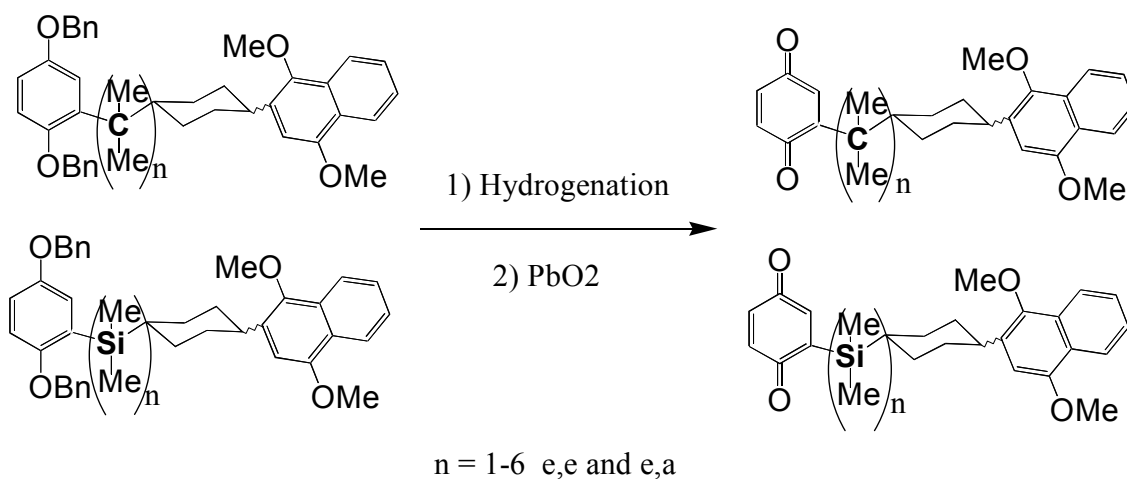
Scheme 6

The resulting alcohol will be transferred to target alkyl chain compounds through dehydration and hydrogenation steps as shown in **Scheme 6**. Another approach for this final assembly for alkyl chain molecules would be to connect the halides with 1,4-cyclohexanedione, mono ethylene ketal first followed by connection with the naphthalene part as shown in **Scheme 7**.



Scheme 7

Scheme 8 shows the final step which is to change dibenzoyloxyphenyl group to quinonyl group and give the final target compounds.

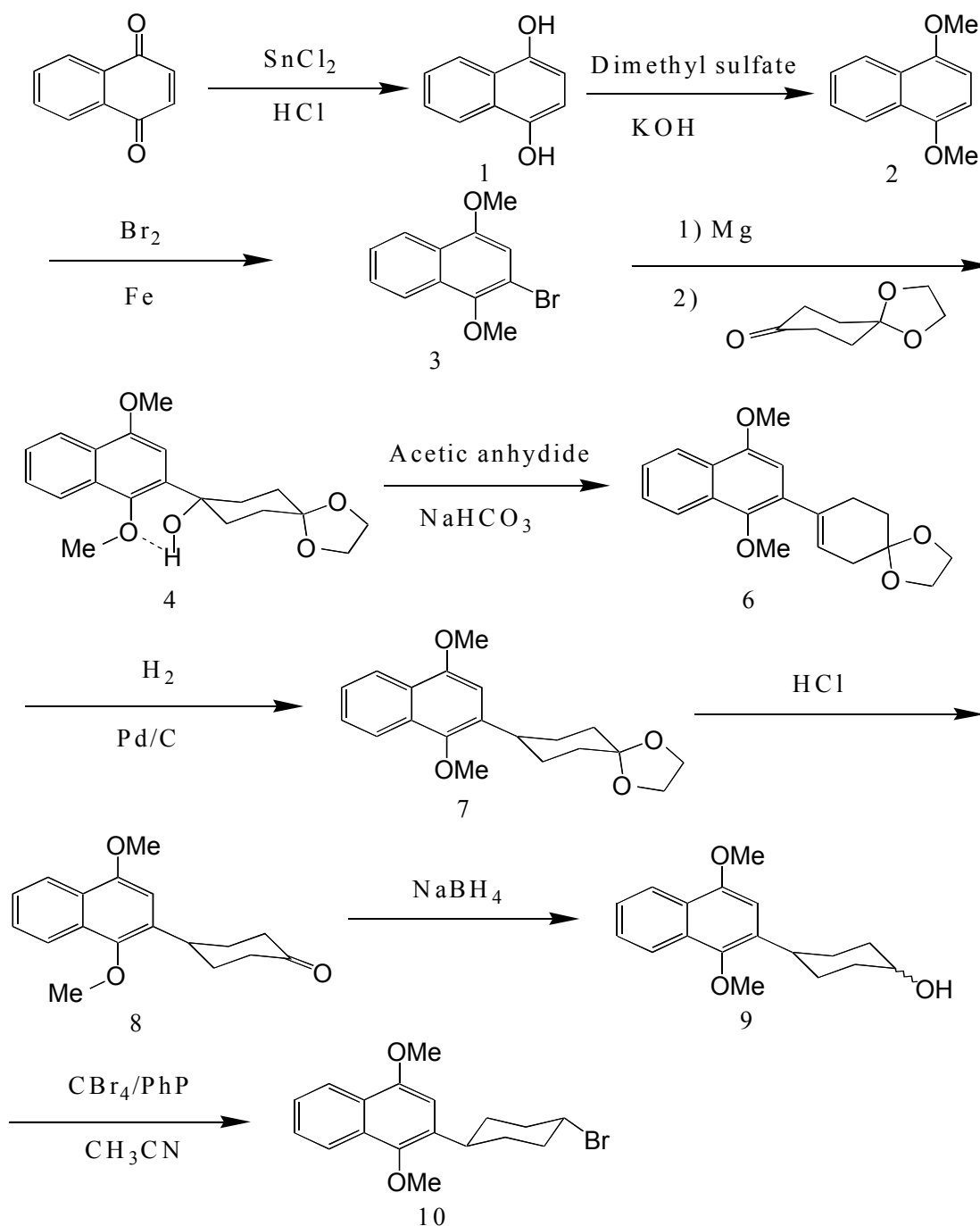


Scheme 8

We will be interested in both e,e- and e,a-1,4-cyclohexanediyl compounds which are thought to be formed in the sequence; these diastereomers should be separable by standard methods.

II.2 Synthetic aspects and characterization of the electron donor precursor

The starting material for the electron-donor part of target molecules was 1,4-dihydroxynaphthalene (**Scheme 9**). This compound (**1**) was commercially provided by Acros Organics, until the end of 1998 when they stopped supplying it. Thereafter



Scheme 9

the chemical (1) was synthesized from 1,4-naphthoquinone through tin(II) chloride reduction in a strong acid [48]. The reaction was done with reported procedures, but at a much lower yield; the cause of the lower yield was never found in our research.

Next 1,4-dihydroxynaphthalene (**1**) was converted to dimethoxynaphthalene (**2**) by methylation with dimethylsulfate under argon or nitrogen protection at a high yield by a known reaction [49].

With suitable amount of iron, 1,4-dimethoxynaphthalene was brominated directly by bromine. The major product was the monobromination product, however some dibromination product also formed that could be removed by column chromatography or vacuum distillation. The Grignard reagent of the resulting bromide (**3**) was reacted with 1,4-cyclohexanedione mono-ethylene ketal to afford alcohol (**4**) [50].

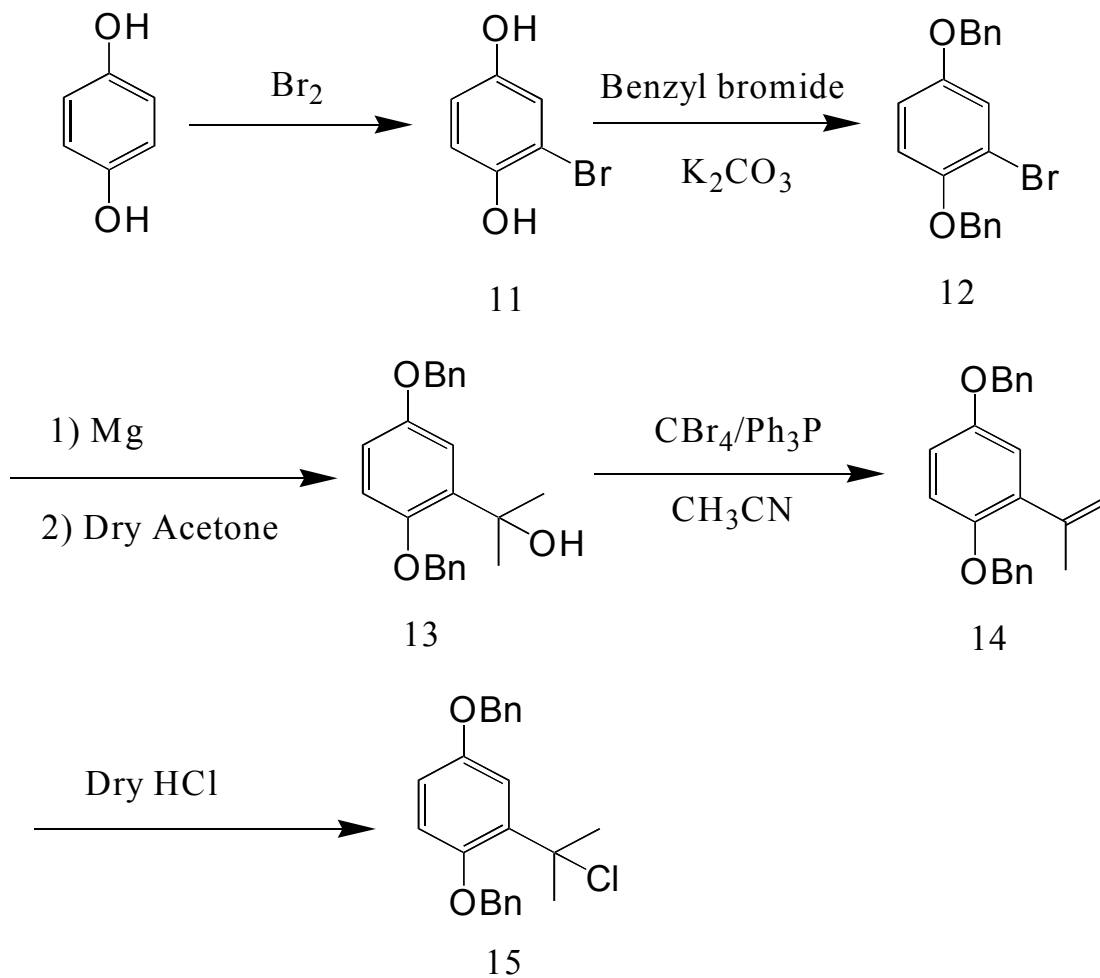
The following dehydration was done through acetic anhydride [51]; it was necessary to modify the reported procedure to prevent acid-catalyzed deprotection of the ether group. Hence sodium bicarbonate was added to the reaction. The olefin (**6**) was hydrogenated by hydrogen under palladium catalyst on activated carbon to give ketal (**7**) [52] in a degassed solvent.

After removing the ethylene ketal protecting group by 5% aqueous HCl and acetone, the remaining ketone group was simply reduced by sodium borohydride [53].

The resulting alcohol (**9**) was thought to be mixture of *cis* and *trans* isomers. It was then changed to bromide (**10**) with CBr₄ and Ph₃P in acetonitrile [54] in good yield. Only one isomer was obtained from column chromatography. However 4-(1,4-dimethoxynaphthyl)cyclohexene (**19**) was also isolated. We believe the olefin (**19**) forms from the *cis* isomer which would favor *e,a* configuration and lose the hydrogen bromide through E₂ elimination mechanism. The *trans* isomer with *e,e* configuration may not eliminate the HBr by this mechanism because there is no hydrogen located in the same plane with bromo group.

II.3 Synthetic aspects and characterization of the electron acceptor precursor

The starting material for the electron acceptor portion of target molecules was 1,4-hydroquinone (**Scheme 10**). The bromination [55] of the hydroquinone was done by bromine. With little dibrominated byproduct, the bromohydroquinone (**11**) was



Scheme 10

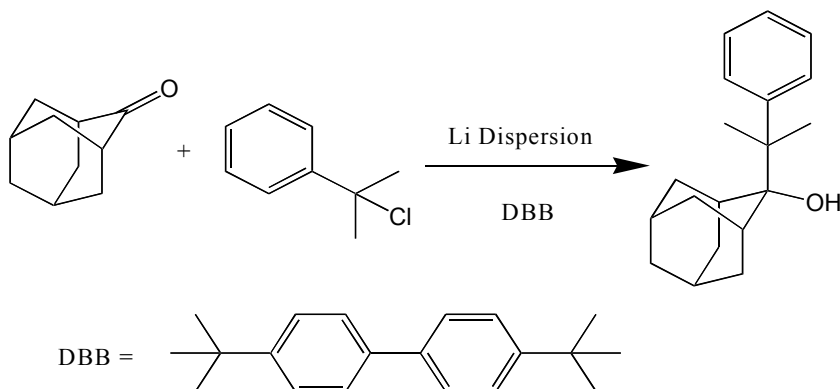
benzylated directly with benzyl bromide and potassium carbonate [56]. Since the product, 1,4-dibenzyloxybromobenzene (**12**) is much less polar than the starting material, the pure product could be obtained by simply filtering the reaction mixture through a short silica gel column and then washing the column with ethyl acetate.

Initial attempts to synthesize the Grignard reagent of the bromide (**12**) were unsuccessful possibly due to the very strong electron-donating groups on the benzene ring. Rodel and Gerlach reported formation of Grignard reagent of 3,5-dibenzoyloxybromobenzene required violent conditions and an unexpectedly long time [57]. Therefore, suitable modification in the reaction time (from the normal 30 minutes to 36 hours) proved to be fruitful in forming the Grignard reagent of (**12**). Because of the same reason, the reaction between acetone and the Grignard reagent took at least 24 hours, however a high yield was achieved.

The direct halogenation of 2-(dibenzoyloxybromophenyl)-2-propanol (**13**) was unsuccessful because the tertiary alcohol (**13**) is sterically hindered and very electron-rich. A quick elimination to form the olefin (**14**) was done by mixing (**13**) with CBr₄ and Ph₃P. The chlorination of the olefin (**14**) was successfully done with hydrogen chloride.

The product chloride (**15**) is very unstable and extremely sensitive to even weak acid and even weak base. It decomposed under vacuum.

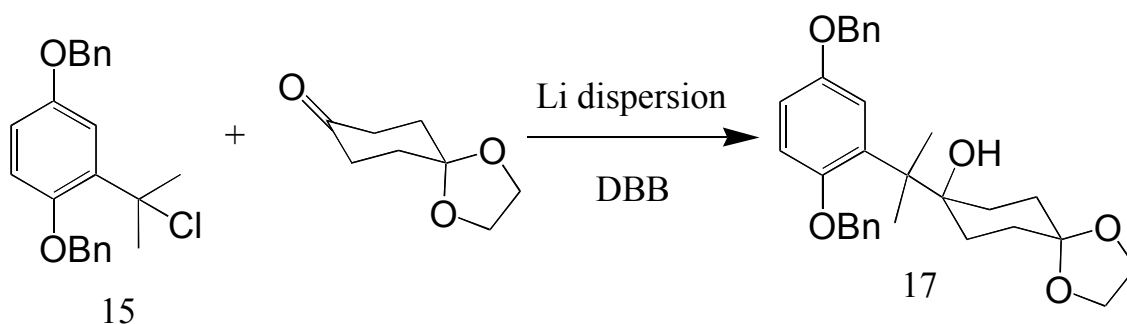
Heajin Choi and his group synthesized 2-cumyladamantan-2-ol in a Barbier-type reaction [58] of adamantanone and cumyl chloride with an electron-transfer agent, 4,4'-di-*t*-butylbiphenyl (DBB) as catalyst (**Scheme 11**) [59].



Scheme 11

The application of electron-transfer agent DBB in my synthesis proved to be a success. Without DBB, I did Barbier lithium reaction of 2-(1,4-dibenzyloxyphenyl)-2-chloropropane (**15**) and two ketones: acetone and 1,4-cyclohexanedione, mono-ethylene ketal. In acetone case, it was successful to give alcohol (**16**) but with very low yield (less than 10%) and in another case, it failed.

After the introduction of catalytic amount of DBB with in the reaction between (**15**) and 1,4-cyclohexanedione, mono-ethylene ketal, a yield of product (**17**) at 43% was obtained (**Scheme 12**).



Scheme 12

Considering Choi's reported yield 67% for the related reaction and instability of the starting chloride (**15**), this yield is reasonable.

II.4 Research for coupling reactions of dimethyldichlorosilane

To gain experience with the silane reactions, the known coupling reactions of bromobenzene's lithium and also Grignard reagents with dimethyldichlorosilane were repeated and high yields of dimethyldiphenylsilane were similar to that reported [60].

When this method was applied on my own coupling reactions of dimethyldichlorosilane with precursors (**10**) and (**12**) as mentioned in **Scheme 3**, the only product was dimethyl-(1,4-dibenzyloxyphenyl)-silanol, which is the hydration

product of dimethyl-(1,4-dibenzyloxyphenyl)-chlorosilane. This product was formed even after a long reflux time (>10h). If bromobenzene was used instead of the bromide (**12**), an asymmetrical silane, dimethylphenyl(1,4-dibenzyloxyphenyl)silane (**18**), was obtained. If cyclohexyl bromide was used instead, there was no coupling product again. A possibility for these failures is that the bromocyclohexyl derivatives are too bulky and can not couple with a silane which already has a bulky substituent.

Indeed for related sterically hindered systems, this Wurtz-type coupling method was limited [61]. We are doing more work for solving this problem now, possibly through the use of more reactive fluorosilanes as starting materials rather than chlorosilanes.

II.5 X-ray Analyses of 4-(1,4-Dimethoxy-2-naphthyl)-4-hydroxycyclohexanone (5**) and its ethylene ketal (**4**)**

After the crystals of (**4**) and (**5**) was raised in benzene, an X-ray structure of each compound were obtained which not only fully identified the chemical but also showed very interesting intramolecular hydrogen bonding formed between the hydroxy group and the proximal methoxy group [50].

The details about this X-ray work are in **appendix A**.

III EXPERIMENTAL

The ^1H - and ^{13}C -NMR spectra were recorded on a Varian Gemini 200 MHz Fourier transform spectrometer (chemical shifts are relative to tetramethylsilane). GC-MS spectra (GC-MS) were recorded on a HP 5790A Spectrometer. The HREI mass spectra

(MS) were obtained from Nebraska Center for Mass Spectrometry, University of Nebraska, Lincoln. The X-ray diffraction analyses were done by Dr. Philip W. Gravelle on an Enraf-Nonius CAD-4 Diffractometer. THF and hexanes were dried by refluxing and distillation over K or Na / benzophenone prior to use. Acetone and acetonitrile was purified with CaSO₄. Elemental analysis was done by Desert Analytics, Tucson, Arizona. All chemicals needed for the syntheses were provided by Aldrich except where noted.

Lithium dispersion was made by vigorously stirring bulk lithium in boiling paraffin oil and subsequently washing with dry hexanes.

Hydrogen chloride was generated by mixing sodium chloride with sulfuric acid and passing the resulting gas through a column filled with granular calcium chloride.

All column chromatography was done with silica gel 60 (230-400 Mesh ASTM) purchased from EM Science. Glass backed preparatory TLC plate (500 µm, indicator F254) was provided by Scientific Absorbents Inc.

1,4-Dihydroxynaphthalene (1):

1,4-naphthoquinone (10 g, 63 mmole) was mixed with 150 ml concentrated hydrochloric acid and 150 ml H₂O. The mixture was heated to 70 °C and SnCl₂ (24 g, 126 mmole) was added cautiously. With magnetic stirring, the mixture was refluxed overnight. After 150 ml H₂O was added, the mixture was filtered while hot and cooled down to 4 °C. Light yellow crystals of the product formed (4 g, 25 mmole, yield 40%). The product decomposed at 183 °C. The product was used directly for the next step without further purification.

1,4-Dimethoxynaphthalene(2) :

Under nitrogen protection and over ice bath, a solution of KOH (2 g, 18 mmole) in degassed H₂O was added dropwise into a mixture of 1,4 dihydroxynaphthalene (4.25 g, 27 mmole) and dimethyl sulfate (15 ml, 158 mmole). After magnetic stirring for 4 h under nitrogen protection, the mixture was filtered through a short silica gel column with ethyl acetate. The organic solutions were combined and solvent was evaporated. The resulting crude product was distilled (5 mm Hg, 110 °C) to obtain the pure product as colorless crystals (4.82 g, 26 mmole, yield 96%).

m.p.: 134°C

¹H NMR (CDCl₃, ppm): 3.97(s, 6H), 6.71(s, 2H), 7.49-7.53(m, 2H), 8.20-8.24(m, 2H).

2-Bromo-1,4-dimethoxynaphthalene(3):

A solution of bromine (0.28 ml, 5 mmole) in 10 ml chloroform was added dropwise to a mixture of 1,4-dimethoxynaphthalene (1 g, 5 mmole) and 30 ml chloroform with iron powder (0.03 g, 0.5 mmole). The resulting mixture was stirred for 6 h. After removing the solvent, the crude product was distilled (5 mm Hg, 180 °C) to offer pure product which was a brown liquid (1 g, 3.8 mmole, yield 76%).

¹H NMR (CDCl₃, ppm): 3.96(s, 3H), 3.98(s, 3H), 6.89(s, 1H), 7.50-7.58(m, 2H), 8.04-8.23(m, 2H).

8-(1,4-Dimethoxy-2-naphthyl)-1,4-dioxaspiro[4.5]decan-8-ol (4)

1,4-dimethoxy-2-bromonaphthalene (1.00 g, 3.74 mmole) was dissolved in dry THF (20 ml). Mg powder (0.25 g, 10.4 mmole) and a small piece of iodine were added and

the resulting mixture was stirred for 0.5 h. Subsequently, a dry THF (15 ml) solution of 1,4-cyclohexanedione mono-ethylene ketal (1.2 g, 7.59 mmole) was added dropwise over 0.5 h. The resulting solution was stirred further for 0.5 h and then poured into ice-cold deionized H₂O (20 ml). The product was extracted with benzene and the resulting benzene extracts were washed with water and then allowed to stand at room temperature. After 3 days, opaque, colorless crystals had formed and were isolated (1 g, 2.92 mmole, 78%).

m.p.: 181-184 °C.

¹H NMR (CDCl₃, ppm): 1.50-2.40 (m, 8H), 3.99(s, 3H), 4.01 (s, 4H), 4.02 (s, 3H), 5.01 (s, 1H), 6.75 (s, 1H), 7.45-7.60 (m, 2H), 7.96-8.02 (m, 1H), 8.18-8.25 (m, 1H).

¹³C NMR (CDCl₃, ppm): 31.06, 36.90, 56.19, 63.92, 64.73, 64.84, 74.24, 76.85, 77.50, 78.16, 102.50, 109.12, 122.32, 122.83, 125.83, 126.44, 127.13, 129.07, 135.33, 147.14, 152.31.

GC-MS: 344 (M⁺).

4-(1,4-Dimethoxy-2-naphthyl)-4-hydroxycyclohexanone (5)

1,4-dimethoxy-2-bromonaphthalene (1.00 g, 3.74 mmole) was dissolved in dry THF (20 ml). Mg powder (0.25 g, 10.4 mmole) and a small piece of iodine were added and the reaction was stirred for 0.5 h. A solution of 1,4-cyclohexanedione mono-ethylene ketal (1.2 g, 7.59 mmole) in THF (15 ml) was then added dropwise. The resulting mixture was then stirred for 0.5 h and finally poured into ice cold 5% aq. HCl (25 ml). After stirring the resulting mixture overnight, the ketone product was extracted with benzene and the resulting benzene extracts were washed with water. The benzene

solution was kept at room temperature for 3 days, after which time opaque, colorless crystals had formed and were isolated (1 g, 3.33 mmole, 89%).

m.p. 166-168°C.

¹H NMR (CDCl₃, ppm): 2.26-2.55 (m, 6H), 2.98-3.21 (m, 2H), 3.98 (s, 3H), 4.05 (s, 3H), 5.47 (s, 1H), 6.65 (s, 1H), 7.45-7.63 (m, 2H), 7.97-8.04 (m, 1H), 8.20-8.27 (m, 1H).

¹³C NMR (CDCl₃, ppm): 37.06, 39.32, 56.15, 63.98, 73.99, 76.86, 77.49, 78.13, 101.79, 122.29, 122.89, 126.16, 126.65, 127.42, 129.06, 133.65, 147.16, 152.62, 212.41.

IR (ν_{max}, KBr): 1716 cm⁻¹ (C=O).

GC-MS: 300 (M⁺).

Anal Calc for C₁₈H₂₀O₄: C, 71.98; H, 6.71. Found: C, 71.67; H, 6.74.

8-(1,4-Dimethoxy-2-naphthyl)-1,4-dioxaspiro[4.5]decan-7-ene (6)

A mixture of 8-(1,4-dimethoxy-2-naphthyl)-1,4-dioxaspiro[4.5]decan-8-ol (**4**) (1 g, 3 mmole), acetic anhydride (20 ml, 275 mmole) and sodium bicarbonate (0.25 g, 3 mmole) was refluxed for 4 h. After the solid was filtered off and the solvent was removed under reduced pressure, pure product as yellow solid (0.74 g, 2.3 mmole, yield 76%) was obtained by column chromatography (eluent: 25% ethyl acetate/hexanes).

¹H NMR (CDCl₃, ppm): 1.96(m, 2H), 2.52(m, 2H), 2.77(m, 2H), 3.82(s, 4H), 3.98(s, 3H), 4.05(s, 3H), 5.64(m, 1H), 5.63(s, 1H), 7.4-7.6(m, 2H), 8.05-8.25(m, 2H).

GC-MS: 326(M⁺)

8-(1,4-Dimethoxy-2-naphthyl)-1,4-dioxaspiro[4.5]decane (7)

In a round bottom flask, 8-(1,4-dimethoxy-2-naphthyl)-1,4-dioxaspiro[4.5]decan-7-ene (6) (1 g, 3 mmole) was dissolved in 25ml THF and then Pd/C (10% Pd content) (0.5 g) was added. The flask was sealed with a balloon filled with hydrogen. The mixture was stirred overnight and it was necessary to refill the balloon several times. After filtering off the solid, the pure product (0.83 g, 2.6 mmole, yield 85%), which is a white solid, was obtained through column chromatography (eluent: 20% ethyl acetate/hexanes).

m.p.: 129-129.5°C

¹H NMR (CDCl₃, ppm): 1.5-2.0(m, 8H), 3.2-3.3(m, 1H), 3.86(s, 4H), 3.98(s, 3H), 4.00(s, 3H), 6.66(s, 1H), 7.35-7.55(m, 2H), 8.00(m, 1H), 8.2(m, 1H).

4-(1,4-Dimethoxy-2-naphthyl)-cyclohexanone (8)

A mixture of 8-(1,4-dimethoxy-2-naphthyl)-1,4-dioxaspiro[4.5]decane (7) (1 g, 3 mmole), acetone (15 ml) and 5% hydrochloric acid (10 ml) was stirred for 4 h. Extra acid was then neutralized through 5% aqueous sodium bicarbonate. The crude product was extracted with ethyl ether. After the solvent was evaporated under reduced pressure, pure product as a white solid (7.7 g, 2.7 mmole, yield 90%) was obtained through column chromatography (eluent: 25% ethyl acetate/hexanes).

m.p.: 139.5-141°C

¹H NMR (CDCl₃, ppm): 2.00-2.30(m, 4H), 2.50-2.80(m, 4H), 3.60-3.80(m, 1H), 3.94(s, 3H), 3.98(s, 3H), 6.60(s, 1H), 7.4-7.6(m, 2H), 8.00(m, 1H), 8.25(m, 1H).

4-(1,4-Dimethoxy-2-naphthyl)-cyclohexanol (9)

4-(1,4-dimethoxy-2-naphthyl)-cyclohexanone (0.5 g, 1.8 mmole) was dissolved in water (10 ml), ethanol (15 ml) and mixed with sodium borohydride (0.3 g, 79 mmole). The resulting mixture was stirred for 4 h. Pure product as white solid (0.45 g, 1.6 mmole, yield 87%) was afforded through column chromatography (eluent: 25% ethyl acetate/hexanes).

¹H NMR (CDCl₃, ppm): 1.40-2.20(m, 8H), 3.10-3.30(m, 1H), 3.65-3.80(m, 1H), 3.86(s, 3H), 3.96(s, 3H), 6.59(s, 1H), 7.35-7.55(m, 2H), 8.00(m, 1H), 8.20(m, 1H)

4-(1,4-Dimethoxy-2-naphthyl)-bromocyclohexane (10)

Carbon tetrabromide (0.52 g, 1.6 mmole) and triphenyl phosphine (0.42 g, 1.6 mmole) were added to a solution of 4-(1,4-dimethoxy-2-naphthyl)-cyclohexanol (0.45 g, 1.6 mmole) in acetonitrile (20 ml). The resulting mixture was stirred overnight. After the solvent was removed under reduced pressure, the pure product (0.50 g, 1.4 mmole, yield 91%) which was a yellow solid was obtained by column chromatography (eluent: 20% ethyl acetate, 10% chloroform in hexanes).

¹H NMR (CDCl₃, ppm): 1.60-2.4(m, 8H), 3.2-3.4(m, 1H), 3.90(s, 3H), 4.06(s, 3H), 4.84(m, 1H), 6.80(s, 1H), 7.40-7.62(m, 2H), 8.0-8.4(m, 2H).

¹³C NMR (CDCl₃, ppm): 28.46(even), 35.58(even), 37.00(odd), 54.939(odd), 56.21(odd), 63.09(odd), 103.11(odd), 122.52(odd), 122.81(odd), 125.38(odd), 127.02(odd), 126.00(even), 129.20(even), 134.80(even), 146.40(even), 152.80(even)

2-Bromo-1,4-hydroquinone (11):

A mixture of bromine (6 ml, 109 mmole) and chloroform (292 ml) was added dropwise to a solution of 1,4-hydroquinone (12 g, 109 mmole) in 436 ml ethyl ether and 168 ml chloroform with magnetic stirring. The resulting mixture was stirred for 10 h at room temperature. After washed with 10% aqueous sodium bicarbonate, the organic solution was dried over MgSO₄. A red solid (20 g, 106 mmole, yield 97%.) was obtained by removing the solvents. The compound was used directly for next step without further purification.

1,4-Dibenzyloxybromobenzene (12):

2-Bromo-1,4-hydroquinone (13 g, 68 mmole) and benzyl bromide (45 ml, 378 mmole) were dissolved to N,N-dimethylformamide (300 ml, 3.86 mole) and then potassium carbonate (55 g, 399 mmole) was added. The mixture was stirred for 1 day and then filtered through a short silica gel column with ethyl acetate. After removing the solvent, a brown solid (23.9 g, 64 mmole, yield 95%) was afforded.

¹H NMR (CDCl₃, ppm): 5.00(s, 2H), 5.09(s, 2H), 6.86(s, 1H), 7.33-7.50(m, 12H).

2-(1,4-Dibenzyloxyphenyl)-2-propanol (13)

Under argon protection, a solution of 1,4-dibenzyloxybromobenzene (**12**) (5 g, 13.5 mmole) in 30 ml dry THF was mixed with magnesium powder (0.5 g, 42 mmole) and then 1, 2-dibromoethane (0.1 ml, 1.1 mmole). The resulting mixture was stirred for 36 h. Acetone (5 ml, 69 mmole) was then injected into the system and the resulting mixture was stirred for another 24 h. After quenching with cold water and filtering the extra

magnesium powder off, the product was extracted with ethyl ether. Yellow crystals (4.7 g, 13.5 mmole, yield 100%) were obtained after removing the solvent.

^1H NMR (CDCl_3 , ppm): 1.62(s, 6H), 4.25(s, 1H), 5.03(s, 2H), 5.11(s, 2H), 6.78-6.84(m, 1H), 6.90-6.94(d, 1H), 7.00-7.62(d, 1H), 7.33-7.47(m, 10H).

^{13}C NMR (CDCl_3 , ppm): 30.25, 71.17, 71.48, 73.07, 113.07, 113.60, 114.82, 128.03, 128.43, 128.74, 129.06, 129.30, 137.00, 137.69, 138.02, 150.98, 153.53.

2-(1,4-Dibenzyloxyphenyl)propene (14)

With vigorous magnetic stirring, carbon tetrabromide (1.18 g, 3.6 mmole) and triphenylphosphine (930 mg, 3.6 mmole) were added to a solution of 2-(1,4-Dibenzyloxyphenyl)-2-propanol (13) (1 g, 2.9 mmole) in acetonitrile (20 ml, 385 mmole). Over the course of 5 minutes, the resulting solution changed from light yellow to dark brown and a precipitate formed. The mixture was then filtered through a short silica gel column with ethyl acetate. After the solvent was removed, the pure product which is a brown solid (0.96 g, 3.6 mmole, yield 100%) was obtained. The product was stored in a vacuum desiccator.

^1H NMR (CDCl_3 , ppm): 1.59(s, 3H), 4.99(s, 2H), 5.01(s, 2H), 5.08-5.14(m, 2H), 6.79-7.03(m, 3H), 7.30-7.40(m, 10H).

2-(1,4-Dibenzyloxyphenyl)-2-chloropropane (15)

2-(1,4-Dibenzyloxyphenyl)propene (**14**) (300 mg, 0.91 mmole) was dissolved in carbon tetrachloride (20 ml). Hydrogen chloride was bubbled into the resulting solution for 30 minutes. After the chloride (**15**) was made, a strong argon stream was introduced to remove the excess hydrogen chloride as well as solvent; the chloride (**15**) was then immediately used in the next step.

Since the product partially decomposed after evaporating the solvent, NMR spectra was obtained when sample was with some original solvent.

^1H NMR ($\text{CDCl}_3/\text{CCl}_4$, ppm): 2.08(s, 6H), 5.02(s, 2H), 5.11(s, 2H), 6.79-6.92(m, 3H), 7.28-7.51(m, 10H).

^{13}C NMR ($\text{CDCl}_3/\text{CCl}_4$, ppm): 33.18, 69.73, 70.74, 71.21, 96.18, 112.35, 113.72, 114.31, 115.42, 115.90, 116.72, 127.27, 127.45, 127.50, 127.56, 127.70, 127.78, 127.80, 127.87, 127.95, 128.47, 128.54, 134.98, 137.20, 137.29, 152.49, 151.00.

2,3-Dimethyl-3-(1,4-Dibenzyloxyphenyl)-2-heptanol (16)

A mixture of 2-(1,4-Dibenzyloxyphenyl)-2-chloropropane (**15**) (300 mg, 0.82 mmole) and acetone (5 ml, 69 mmole) in 15 ml dry THF was added dropwise into a lithium dispersion (1 g, 143 mmole) in 10 ml dry THF at 0 °C. The resulting mixture was stirred for 24 h. After quenching with ice cold brine, the crude product was extracted by ethyl ether. Pure product as a yellow solid (30 mg, 0.077 mmole) was afforded through preparatory TLC plate. Overall yield from (**14**) was 8.2%.

^1H NMR (CDCl_3 , ppm): 1.26(d, 6H), 1.52(d, 6H), 4.84(s, 2H), 5.02(s, 2H), 6.55-6.95(m, 3H), 7.27-7.45(m, 10H)

^{13}C APT NMR (CDCl_3 , ppm): 25.75(odd), 26.78(odd), 29.80(odd), 70.67(even), 70.98(even), 72.04(even), 72.30(even), 112.17(odd), 112.46(odd), 112.99(odd), 114.25(odd), 118.47(odd), 127.45(odd), 127.59(odd), 127.86(odd), 128.16(odd), 128.49(odd), 128.73(odd), 136.50(even), 137.40(even), 152.80(even).
MS: 390(M^+)

8-(1-(1,4-Dibenzyloxy-2-phenyl)-methylethyl)-1,4-dioxaspiro[4.5]decan-8-ol (17)

After 2-(1,4-Dibenzyloxyphenyl)-2-chloropropane (**15**) (300 mg, 0.82 mmole) was made, a strong argon stream was introduced to remove the solvent and trace hydrogen chloride. A lithium dispersion (1 g, 143 mmole) was made in the same method as mentioned before during the time. When the solvent of the chloride fully evaporated, the residue and 1,4-cyclohexanedione mono ethylene ketal (312 mg, 2 mmole) were dissolved in 20 ml dry THF. At 0 °C, the resulting solution was added dropwise with vigorous stirring to a mixture of the lithium dispersion and 4,4'-di-*tert*-butylbiphenyl (30 mg, 0.1 mmole) in 15 ml THF at a rate to maintain the dark-green color of the radical anion. Following overnight stirring at room temperature, the mixture was quenched with ethanol. Pure product as a yellow solid (220 mg, 0.45 mmole) was afforded through preparatory TLC plate. Overall yield from (**14**) was 48%.

^1H NMR (CDCl_3 , ppm): 1.2-2.1(m, 14H), 3.91(s, 4H), 5.00(s, 2H), 5.10(s, 2H), 6.72-7.00(m, 3H), 7.30-7.48(m, 10H)

^{13}C APT NMR (CDCl_3 , ppm): 25.60(odd), 28.91(odd), 30.52(even), 30.93(even), 46.76(even), 64.05(even), 70.65(even), 72.11(even), 74.86(even), 109.15(even), 112.58(odd), 114.78(odd), 118.50(odd), 127.43(odd), 127.52(odd), 127.61(odd),

127.90(odd), 128.18(odd), 128.55(odd), 128.76(odd), 136.44(even), 136.94(even),
137.20(even), 151.40(even), 153.00(even)

MS: 488(M⁺)

Dimethylphenyl(1,4-dibenzyloxyphenyl)silane (18)

A solution of 1,4-Dibenzyloxybromobenzene (0.5 g, 1.33 mmole) and dimethyldichlorosilane (0.15 ml, 1.33 mmole) in 15 ml dry THF was mixed with magnesium (1 g, 42 mmole) under argon protection. The mixture was stirred for 36 h. Then bromobenzene (0.24 g, 1.5 mmole) which was dried over CaSO₄ was measured by a syringe and was injected into the mixture. After stirring for another 24 h, the mixture was filtered through a short silica gel column with ethyl acetate. Yellow crystals (0.55 g, 1.30 mmole, yield 97%) were afforded by column chromatography (eluent: 5% ethyl acetate/hexanes).

¹H NMR (CDCl₃, ppm): 0.54(s, 6H), 4.94(s, 2H), 4.98(s, 2H), 6.70-7.50(m, 3H), 7.15-7.60(m, 15H).

¹³C APT NMR (CDCl₃, ppm): 2.26(odd), 70.37(even), 70.68(even), 111.46(odd), 115.88(odd), 116.30(odd), 123.18(odd), 127.44(odd), 127.56(odd), 127.83(odd), 128.31(odd), 128.51(odd), 128.73(odd), 134.19(odd), 137.22(even), 137.36(even), 138.64(even), 152.75(even), 157.80(even).

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